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From coal to biomass gasification: Comparison of thermodynamic efficiency

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Abstract

The effect of fuel composition on the thermodynamic efficiency of gasifiers and gasification systems is studied. A chemical equilibrium model is used to describe the gasifier. It is shown that the equilibrium model presents the highest gasification efficiency that can be possibly attained for a given fuel. Gasification of fuels with varying composition of organic matter, in terms of O/C and H/C ratio as illustrated in a Van Krevelen diagram, is compared. It was found that exergy losses in gasifying wood (O/C ratio around 0.6) are larger than those for coal (O/C ratio around 0.2). At a gasification temperature of 927 °C, a fuel with O/C ratio below 0.4 is recommended, which corresponds to a lower heating value above 23 MJ/kg. For gasification at 1227 °C, a fuel with O/C ratio below 0.3 and lower heating value above 26 MJ/kg is preferred. It could thus be attractive to modify the properties of highly oxygenated biofuels prior to gasification, e.g. by separation of wood into its components and gasification of the lignin component, thermal pre-treatment, and/or mixing with coal in order to enhance the heating value of the gasifier fuel.

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1. Introduction

Gasifiers can be designed to gasify almost any kind of organic feed. A wide variety of fuels, such as many types of wood, agricultural residues, peat, coal, anthracite, oil residues and municipal solid waste may be considered. During the oil crisis in the late 1970s and through to the middle of the 1980s, coal was regarded as a very important substitute for oil. Reserves of coal are abundant and more geographically spread over the world than crude oil. In this period, several coal gasifiers were developed and commercialized. However, due to a large drop in the oil price, coal gasification did not gain a much larger share of the energy market, although heavy oil gasification is commercially practiced at several refineries.

During the last decennium, there has been renewed interest in gasification. Focus is less on coal, but more on biomass gasification as a form of renewable energy. Introduction of biomass as a renewable energy source is vital for the transition to a more sustainable society. An example for the shift from coal to biomass is the power station in Buggenum, the Netherlands, which integrates coal gasification and combined cycle technology. Recently, a decision was made to co-gasify up to 50% of biomass in order to generate a high proportion of 'green energy' [1]. The Kyoto protocol emphasizing the need to combat carbon dioxide emission has also been an impetus for the interest in biomass gasification. Carbon dioxide emissions from using biomass as a fuel are perceived as neutral because this carbon dioxide is fixed by photosynthesis in a relatively short period. Nevertheless, it has been argued that society should try to use biomass with the same thermodynamic efficiency as fossil fuels, regardless of its perceived CO_2-neutrality [2]. It is important from an energy saving and environmental point of view to find out whether biomass can be gasified with the same efficiency as coal.

An interesting difference between coal and biomass lies in the composition of their organic matter: woody biomass contains typically around 50 wt% carbon and 45 wt%

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Nomenclature

C	mole fraction of carbon
H	mole fraction of hydrogen
I	irreversibility (MJ/s); subscript indicates the type of (sub-) process
$\mathrm{HHV}_{\mathrm{fuel}}$	higher heating value of fuel (MJ/kg)
$\mathrm{LHV}_{\mathrm{fuel}}$	lower heating value of fuel (MJ/kg)
O	mole fraction of oxygen
z_{A}	weight fraction of ashes (wt% dry)
z_{C}	weight fraction of carbon (wt% dry)
z_{H}	weight fraction of hydrogen (wt% dry)
z_{N}	weight fraction of nitrogen (wt% dry)
z_{O}	weight fraction of oxygen (wt% dry)
z_{S}	weight fraction of sulfur (wt% dry)
β	ratio of chemical exergy and lower heating value of fuel [-]
$\varepsilon_{\mathrm{ch,fuel}}$	chemical exergy of fuel (MJ/kg)
$\varepsilon_{\mathrm{ch,fuel\_unconv}}$	chemical exergy of unconverted fuel (MJ/kg)
$\varepsilon_{\mathrm{ch,oxygen}}$	chemical exergy of oxygen (MJ/kg)
$\varepsilon_{\mathrm{ch,steam}}$	chemical exergy of steam (MJ/kg)
$\varepsilon_{\mathrm{ch,gas}}$	chemical exergy of gas (MJ/kg)
$\varepsilon_{\mathrm{ph,fuel\_unconv}}$	physical exergy of unconverted fuel (MJ/kg)
$\varepsilon_{\mathrm{ph,steam}}$	physical exergy of steam (MJ/kg)
$\varepsilon_{\mathrm{ph,gas}}$	physical exergy of gas (MJ/kg)
$\Phi_{m,\mathrm{fuel}}$	mass flow of fuel (kg/s)
$\Phi_{m,\mathrm{fuel\_unconv}}$	mass flow of unconverted fuel (kg/s)
$\Phi_{m,\mathrm{oxygen}}$	mass flow of oxygen (kg/s)
$\Phi_{m,\mathrm{steam}}$	mass flow of steam (kg/s)
$\Phi_{m,\mathrm{gas}}$	mass flow of gas (kg/s)
Ψ	exergetic efficiency

oxygen, whereas coal contains (depending on coal rank) 60–85 wt% carbon and 5–20 wt% oxygen. One might argue that the high oxygen content of biomass is beneficial because less oxygen needs to be added for gasification; on the other hand, biomass has a relatively low calorific value, which would not be beneficial for gasification. The fundamental question which fuel composition is more advantageous for gasifiers is addressed in this study.

The evaluation of gasification efficiency is based on exergy analysis (formerly known in the USA as availability analysis). The exergetic efficiency is based on the first as well as the second law of thermodynamics, which is useful because it considers not only the decrease in energy of combustion of the product gas compared to the solid fuel (due to partial oxidation) but also increases in entropy (as a solid fuel is decomposed into many smaller molecules). In the 1980s, exergy analysis was applied to evaluate coal gasification processes [3–5]. Later, biomass gasifiers were analyzed [6–8]. These analyses show that second-law efficiencies are considerably lower than first-law efficiencies, e.g. for a coal gasifier, the first-law efficiency is nearly 100% for a well-insulated gasifier with negligible heat losses, whereas the second-law efficiency equals 79% [3]. However, the results of these analyses are difficult to compare because the gasification processes are not always analyzed on the same basis, e.g. both autothermal and allothermal gasifiers have been considered, complete and incomplete carbon conversions, etc. Therefore, this paper comprises a comprehensive analysis of the effect of the fuel type and related fuel composition on the efficiency that can be attained in a gasifier.

The paper starts with a description of the applied methodology, notably: which fuels are considered, what their thermodynamic properties are, and how the gasification efficiency is defined. As a chemical equilibrium model is applied throughout this study to describe the performance of gasifiers, its main assumptions and their validity for practical gasifiers is considered in a separate section. It is demonstrated that the equilibrium model indicates the maximum efficiency that can possibly be attained when gasifying a fuel. Finally, results are given that compare the attainable gasification efficiency for the various fuels considered.

2. Methodology

2.1. *Gasifier fuel properties*

As a gasifier fuel, biomass and coal vary in many properties, such as their heating values, proximate analyses (fixed carbon, volatile material, ash content and moisture content), ultimate analyses (amounts of carbon, hydrogen, oxygen, sulfur, nitrogen, chloride and other impurities) and sulfur analyses (type of sulfur present). For example, the organic matter in biomass contains a large fraction of volatile material, namely 70–80 wt%. Coals range from lignite with approximate volatile matter of 27% to anthracite with an average of 5%, with sub-bituminous and bituminous coals intermediate between these values.

The change in composition from biomass to coal is illustrated using a diagram developed by Van Krevelen [9]. Fig. 1 shows the change in atomic ratios H/C and O/C from biomass to peat, lignite, coal and anthracite. The figure specifically shows the composition of lignocellulose, i.e. wood, since this is the most abundant biofuel. Wood is related to coal because it is the precursor for its formation in nature by various coalification processes. Vitrinite, the most important constituent of coal, descends from woody tissue [9]. This paper aims to compare gasification efficiencies that can be attained for all fuels mentioned in the Van Krevelen diagram. Focus is on the composition of the organic material in the fuel, i.e. on dry and ash-free fuels, taking into account only the most important constituents: carbon, hydrogen and oxygen.

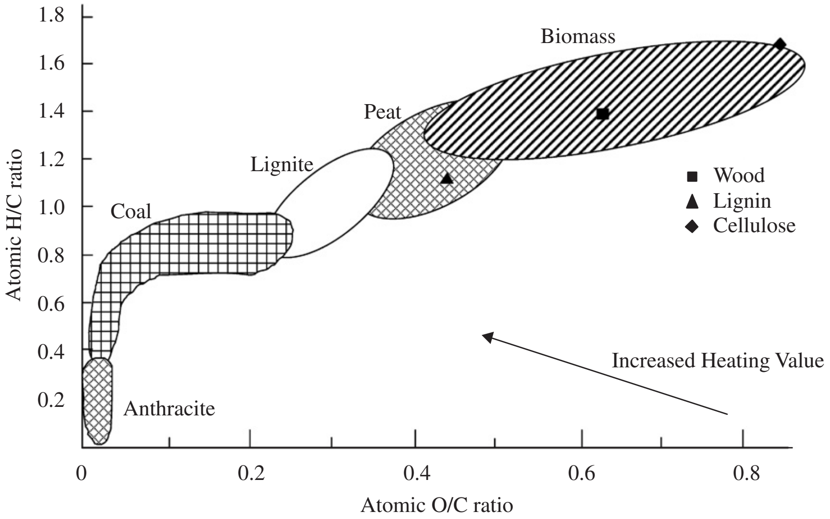

Fig. 1. Van Krevelen diagram for various solid fuels.

In order to perform thermodynamic calculations for reacting fuels with oxygen, their thermodynamic properties must be available, such as the heating values and chemical exergies (or alternatively, enthalpy and entropy of formation). Thermodynamic properties of most fuels are not exactly known, except those for cellulose, because the structure of these fuels is not well defined. Statistical correlations are used to overcome this problem. The higher heating value can be accurately predicted by the correlation developed by Channiwala and Parikh (in MJ/kg) [10]:

$$\mathrm{HHV}_{\mathrm{fuel}} = 0.3491 z_{\mathrm{C}} + 1.1783\, z_{\mathrm{H}} - 0.1034\, z_{\mathrm{O}} - 0.0151 z_{\mathrm{N}} + 0.1005 z_{\mathrm{S}} - 0.0211 z_{\mathrm{A}}. \quad (1)$$

This equation was developed for a wide spectrum of fuels, including the whole range from coal to biomass. It has a standard deviation from experimentally determined values of only 1.45% and the bias error is negligible. Since the gasifier is regarded as a CHO system, only the first three terms apply. The higher heating value is converted to lower heating value using the enthalpy of evaporation for water formed during combustion. Finally, the statistical correlation of Szargut and Styrylska [11] was used to calculate the chemical exergy of the fuel:

$$\varepsilon_{\mathrm{ch,\,fuel}} = \beta\, \mathrm{LHV}_{\mathrm{fuel}}, \quad (2)$$

with

$$\beta = 1.0438 + 0.0158 \tfrac{H}{C} + 0.0813 \tfrac{O}{C} \quad \text{for } \tfrac{O}{C} \leqslant 0.5, \quad (3)$$

$$\beta = \frac{1.0414 + 0.0177(H/C) - 0.3328(O/C)\left[1 + 0.0537(H/C)\right]}{1 - 0.4021(O/C)} \quad \text{for } 0.5 < \tfrac{O}{C} \leqslant 2. \quad (4)$$

Fig. 2 displays the lower heating values and the ratios of chemical exergies to lower heating values as a function of the fuel composition shown in the Van Krevelen diagram. The effect of H/C ratio on these parameters is much smaller than that of the O/C ratio. Therefore, they are plotted only as a function of O/C ratio with the area representing realistic H/C ratios, as these occur in the Van Krevelen diagram. This approach is also followed in the rest of this paper. Obviously, fuels with high O/C ratio have a smaller heating value than those with low O/C ratio. However, the factor β increases with increasing O/C ratio, which indicates that by decomposing a fuel with high O/C ratio, relatively more work may be delivered. This effect is known from structurally well-defined compounds, e.g. when comparing the ratio between chemical exergy and lower heating value for methane (O/C of 0) and methanol (O/C of 1). For methane, this ratio is 1.037 (831.65 kJ/mol/802.33 kJ/mol), whereas for methanol the ratio is 1.125 (718/638.4).

2.2. *Gasification efficiency*

The gasification efficiencies are determined for a gasifier as well as a gasification system. For the gasifier, shown in Fig. 3a, the thermodynamic efficiency is defined as the exergy increase of the gas divided by the exergy decrease of the solid fuel. The efficiency of gasifying a fuel with pure oxygen and optionally steam is therefore given by

$$\Psi_{\mathrm{gasifier}} = \frac{\begin{array}{c}\left(\Phi_{\mathrm{m,gas}}\left(\varepsilon_{\mathrm{ch,gas}} + \varepsilon_{\mathrm{ph,gas}}\right)\right. \\ -\Phi_{\mathrm{m,oxygen}}\varepsilon_{\mathrm{ch,oxygen}} \\ \left.-\Phi_{\mathrm{m,steam}}\left(\varepsilon_{\mathrm{ch,steam}} + \varepsilon_{\mathrm{ph,steam}}\right)\right)\end{array}}{\begin{array}{c}\left(\Phi_{\mathrm{m,fuel}}\varepsilon_{\mathrm{ch,fuel}}\right. \\ -\Phi_{\mathrm{m,fuel\_unconv}} \\ \left.\times\left(\varepsilon_{\mathrm{ch,fuel\_unconv}} + \varepsilon_{\mathrm{ph,fuel\_unconv}}\right)\right)\end{array}}. \quad (5)$$

The chemical exergy of all gaseous components is obtained from Szargut et al. [12]. For the calculation of physical exergy, it is essential to use accurate data for the enthalpy and entropy in order to obtain accurate results. Thermodynamic data depend on the heat capacity as a

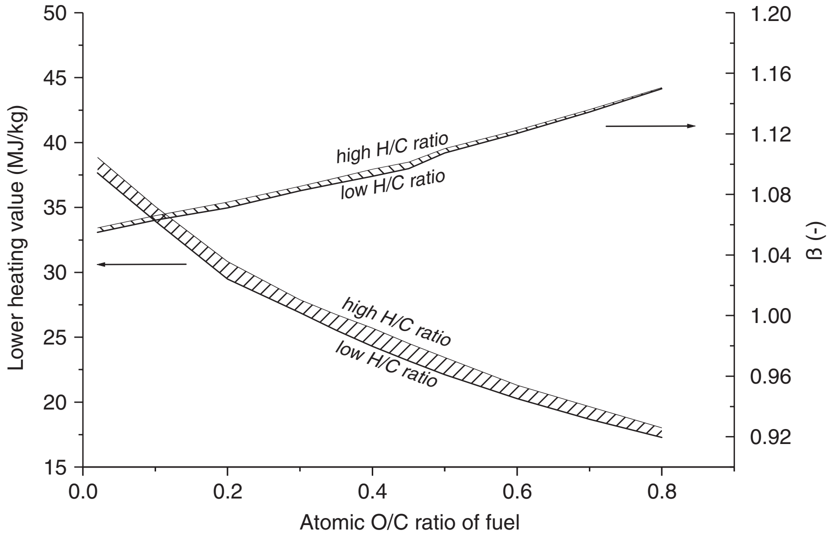

Fig. 2. Lower heating value and ratio of chemical exergy to lower heating value of fuels shown in the Van Krevelen diagram.

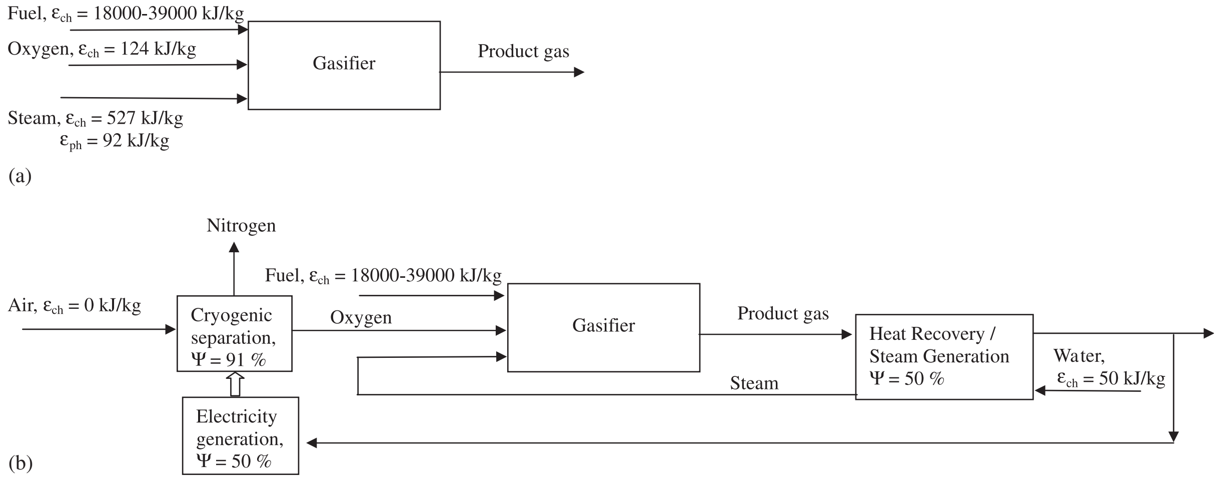
Fuel, ε_{ch} = 18000-39000 kJ/kg
Oxygen, ε_{ch} = 124 kJ/kg
Gasifier
Product gas
Steam, ε_{ch} = 527 kJ/kg
ε_{ph} = 92 kJ/kg
(a)
Nitrogen
Fuel, ε_{ch} = 18000-39000 kJ/kg
Air, ε_{ch} = 0 kJ/kg
Cryogenic separation, Ψ = 91 %
Oxygen
Gasifier
Product gas
Heat Recovery / Steam Generation Ψ = 50 %
Water, ε_{ch} = 50 kJ/kg
Steam
Electricity generation, Ψ = 50 %
(b)

Fig. 3. (a) Block diagram of a gasifier. (b) Block diagram of a gasification system, including production of oxygen, steam and electricity.

function of temperature. Commonly used third-order polynomial equations give large deviations at temperatures above 1000 K. To overcome this problem, a more advanced equation developed by Barin [13] is used for all components. The physical exergy of the product gas consists only of a temperature-dependent term, i.e. the work content of the sensible heat of the product gas. A pressure-dependent term is not included because gasification at atmospheric pressure is considered.

The gasifier is part of a gasification system, shown in Fig. 3b, which includes steam, oxygen and electricity production units. Since these units consume exergy, irreversibilities also take place outside of the gasifier. To enable a fair comparison between all fuels, the above-mentioned efficiencies have to be corrected with the irreversibilities occurring in these production units. This correction is done on the basis that electricity required for oxygen production and process steam are generated from gasification product gas. This leads to the following definition:

$$\Psi_{\text{system}} = \frac{\begin{array}{c}\big(\Phi_{\text{m,gas}}\left(\varepsilon_{\text{ch,gas}} + \varepsilon_{\text{ph,gas}}\right)\\ -I_{\text{oxygen\_production}} - I_{\text{electricity\_production}}\\ -I_{\text{steam\_production}}\big)\end{array}}{\begin{array}{c}\big(\Phi_{\text{m,fuel}}\varepsilon_{\text{ch,fuel}} - \Phi_{\text{m,fuel\_unconv}}\\ \times\left(\varepsilon_{\text{m,fuel\_unconv}} + \varepsilon_{\text{m,fuel\_unconv}}\right)\big)\end{array}}. \tag{6}$$

For large-scale oxygen production, cryogenic separation of air is the most widely applied process. The electricity consumption of large-scale cryogenic oxygen plants is approximately 380 kWh/t oxygen [14]. This is equivalent to an exergetic efficiency of 9.1%. Electricity required for oxygen production can be generated from gasification product gas in gas turbines or fuel cells; an exergetic efficiency of 50% is assumed for this process. Steam can be produced by heat exchange with the product gas. This study considers steam at 500 K and atmospheric pressure.

This relatively low steam quality is preferably produced by heat exchange with product gas, rather than in a boiler. For a well-designed heat exchanger, a thermodynamic efficiency of 50% can be achieved. Finally, the exergy of air and water, required for oxygen and steam production, is negligible.

This paper also uses the so-called chemical efficiency, which is calculated by neglecting the physical exergy of product gas in Eq. (5) and/or Eq. (6). The chemical efficiency indicates how well the chemical exergy of fuel is preserved in the chemical exergy of product gas.

2.3. Process losses

To gain more understanding of the observed thermodynamic efficiency, it is possible to analyze the various subprocesses occurring in a gasifier. This methodology is described in more detail in [15]. Gasification is conceptually assumed to be a sequence of the following steps: heating of solid fuel and reactant gases to the gasification temperature, mixing of reactant gases, instantaneous chemical reaction, heat transfer to the reactant molecules, and product mixing. The rate of heat transfer determines at which temperature the chemical reaction takes place. If heat transfer is very fast, the gasifier is isothermal so that the product molecules have the same temperature as the reactant molecules. However, if heat transfer is slow, the temperature of product molecules may be much higher than the reactant molecules. For practical purposes, only the isothermal case is considered here.

For each sub-process, the irreversibilities can be calculated. The overall irreversibilities equal the sum of the irreversibilities of the subprocesses:

$$\begin{aligned} I_{\text{overall}} = {} & I_{\text{heating\_fuel}} + I_{\text{heating\_O}_2} \\ & + I_{\text{heating\_steam}} + I_{\text{reactant\_mixing}} \\ & + I_{\text{chemical\_reaction}} + I_{\text{product\_mixing}}. \end{aligned} \tag{7}$$

The irreversibilities for heating of the solid fuels cannot be calculated separately because the heating capacities of complex fuels are not known as a function of temperature, and also pyrolysis takes place when these fuels are heated. Therefore, the irreversibilities for heating of fuel and chemical reaction are combined. The irreversibilities can be divided by the expended exergy, so that they are expressed as relative exergy losses. The sum of these relative exergy losses is the fraction of the expenditures lost through irreversibility. Irreversibilities occurring in oxygen, electricity and steam production unit gasification systems can also be taken into account as relative exergy losses.

3. Gasifier models

3.1. Equilibrium model

A chemical equilibrium model is applied to predict the product gas composition, gas amount and carbon conversion in gasifiers. Equilibrium models are valuable because they predict the thermodynamic limits of the gasification reaction system. The equilibrium model has been extensively documented in literature [16–19] and applied for performance evaluations [20,21]. However, it remains important to realize that the main assumptions behind this model may not always be valid for practical gasifiers. These assumptions are discussed below:

- The gasifier is often regarded as a perfectly insulated apparatus, i.e. heat losses are neglected. In practice, gasifiers have heat losses to the environment, but this term can be incorporated in the enthalpy balance of the equilibrium model.
- Perfect mixing and uniform temperature are assumed for the gasifier. Different hydrodynamics are observed in practice, depending on the design of the gasifier. Gasification technologies utilize fixed bed, moving bed, fluidized bed or entrained bed reactors, in which the contacting pattern of gas and solid, and their residence times differ. For example, if wood is gasified in a countercurrent moving bed gasifier, devolatilization takes place before the particles reach the hot zone in the bottom of the gasifier, volatiles are contained in the product gas stream, and the composition of this gas stream will be very different from the equilibrium composition. In a cocurrent moving bed gasifier, these volatiles pass through a narrow cross-section, the so-called throat, in which the temperature is high. The equilibrium model has much better predictive potential for this gasifier [22]. The fluid dynamics of large-scale gasifiers, such as fluidized bed and entrained flow gasifiers, are more favorable than for moving bed gasifiers, but the residence time of the solids is much shorter.
- The model assumes that gasification reaction rates are fast enough and residence time is sufficiently long to reach the equilibrium state. The kinetics of gasification reactions is complicated: in the gasifying process, thermal pyrolysis, homogeneous gas phase and heterogeneous gas–solid reactions take place, so that thousands of chemical reactions may occur [19]. Although it is difficult to determine the intrinsic kinetics of these reactions, many researchers agree that steam and carbon dioxide reforming reactions of char are kinetically limited at gasification temperatures lower than 1000 °C [23]. Furthermore, the product gas of fluidized bed gasifiers generally contains tar, which is not considered in equilibrium models, and much more hydrocarbons (especially methane) than predicted. For entrained flow gasifiers, which operate at temperatures in the range 1050–1400 °C, the approach to equilibrium is much better. E.g., for a Shell coal gasifier, all predicted gas species are within 0.7% absolute of the measured values, and equilibrium temperatures are very close to the gasifier exit temperatures [24].

Table 1 summarizes all the assumptions on which this study was based.

Table 1
Simplifying assumptions in this study

Fuel	• C–H–O considered with varying composition as in Van Krevelen diagram • Presence of nitrogen, sulfur, minerals and ashes is ignored • Higher heating value and chemical exergy of fuel estimated by empirical correlations
Gasifying agent	• Pure oxygen (O_2), in some cases together with steam (H_2O)
Operating conditions	• Atmospheric pressure • Negligible heat losses
Gasifier	• Perfect mixing • No kinetic limitations, i.e. chemical equilibrium is reached • Complete carbon conversion
Thermodynamic efficiency	• Gasifier efficiency • System efficiency, which incorporates irreversibilities incurred in production of oxygen, steam and electricity (for which realistic values are assumed)

3.2. *'Quasi'-equilibrium models*

In order to describe the behavior of fluidized bed gasifiers more accurately, modifications have been made to the equilibrium model. Empirical parameters have been added, such as the amount of methane in the product gas [25] and/or the carbon conversion [26]. Inclusion of empirical parameters leads to a better agreement with experimental data, but the model looses much of its predictive capabilities.

Another approach is the use of quasi-equilibrium temperatures, whereby the equilibria of the reactions defined in the model (see Eqs. 8–10) are evaluated at a temperature, which is lower than the actual process temperature.

$$C + 2H_2 = CH_4, \tag{8}$$

$$C + H_2O = CO + H_2, \tag{9}$$

$$C + CO_2 = 2CO. \tag{10}$$

This approach was introduced by Gumz [16]. For fluidized bed gasifiers, the average bed temperature can be used as the process temperature, whereas for downdraft gasifiers, the outlet temperature at the throat exit should be used. Li et al. [26] found that the kinetic carbon conversion for pressurized gasification of subbituminous coal in the temperature range 747–877 °C is seen to be comparable to equilibrium predictions for a temperature about 250 °C lower. Bacon [27] defined quasi-equilibrium temperatures for each independent chemical reaction. Based on 75 operational data points measured in circulating fluidised bed (CFB) gasifiers operated on biomass, Kersten [23] has shown that for operating temperatures in the range 740–910 °C, the reaction equilibria of Eqs. (8)–(10) should be evaluated at much lower temperatures (respectively, $457 \pm 29\,^{\circ}C$, $531 \pm 25\,^{\circ}C$, and $583 \pm 25\,^{\circ}C$). These quasi-equilibrium temperatures appear to be independent of process temperature in this range.

An important subject, which has not yet been studied thoroughly in the gasification literature, is whether kinetic limitations increase or decrease the efficiency of gasifiers. To this end, Appendix A compares gasification at equilibrium conditions with quasi equilibrium conditions. The conclusion is reached that the gasification efficiency is severely affected when the gasification reactions of Eqs. (9) and (10) are kinetically limited and do not contribute sufficiently to the carbon conversion. The equilibrium model therefore indicates the maximum efficiency that can possibly be attained when gasifying a fuel. This model is applied in the next section to study the effect of changes in fuel composition on the maximum gasification efficiency. As a word of caution, it must be realized that it is difficult to reach this maximum at gasification temperatures below 1000 °C, even for reactive fuels such as biomass. This may require operation at prolonged residence times (e.g., in a bubbling fluidized bed, the carbon conversion appears to be higher than in a CFB [23]), higher pressures to increase the char reforming rates (although less favorable for the equilibrium of these reactions), which is demonstrated by the relatively high carbon conversion of the Värnamö gasifier [28], and/or catalytically active bed materials such as dolomite or olivine [29].

4. Results

4.1. *Gasification temperatures and equivalence ratios*

The gasification efficiency that can be achieved as a function of fuel composition is evaluated at three different temperatures: the carbon boundary temperature (the temperature obtained when exactly enough oxygen is added to achieve complete gasification), and reference temperatures of 927 and 1227 °C. The reference temperature of 927 °C is beneficial to preserve the chemical exergy of the fuel in the product gas [21]. However, it is evident from the previous section that higher temperatures may very well be required in practice, in order to reduce kinetic limitations. Therefore, a temperature of 1227 °C is also included as a reference temperature. Fig. 4 shows the carbon boundary temperatures for gasification of fuels with different O/C and H/C ratios, as well as the reference temperatures. It can be observed that lower oxygen content in the fuel corresponds to a higher carbon boundary temperature. Optimum gasification temperatures were found to increase from 782 °C for biomass (average composition $CH_{1.4}O_{0.6}$) to 1668 °C for gasification of coal (average composition $CH_{0.95}O_{0.2}$) gasification.

Fig. 5 shows the equivalence ratio required, depending on the desired gasification temperature, for different O/C and H/C ratios of the fuel. The equivalence ratio expresses the amount of oxygen required for gasification relative to the amount required for combustion. Equivalence ratios may range from 0.244 for cellulose to 0.500 for pure carbon (graphite), as exemplified in the equations below:

Cellulose gasification:

$$C_6(H_2O)_5 + 1.461\,O_2 = 4.567CO + 1.295CO_2 + 0.138CH_4 + 3.958H_2 + 0.766H_2O. \tag{11}$$

Cellulose combustion:

$$C_6(H_2O)_5 + 6O_2 = 6CO_2 + 5H_2O. \tag{12}$$

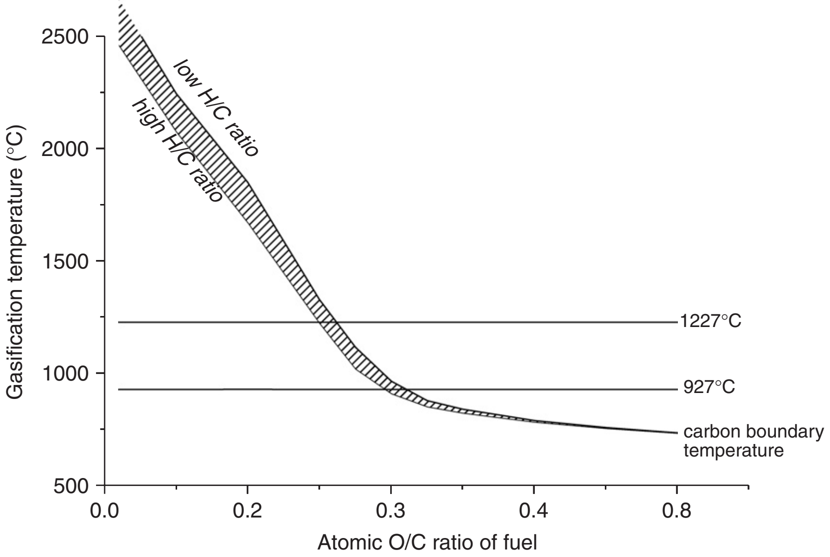

Fig. 4. Gasification temperatures for fuels of varying O/C and H/C ratios.

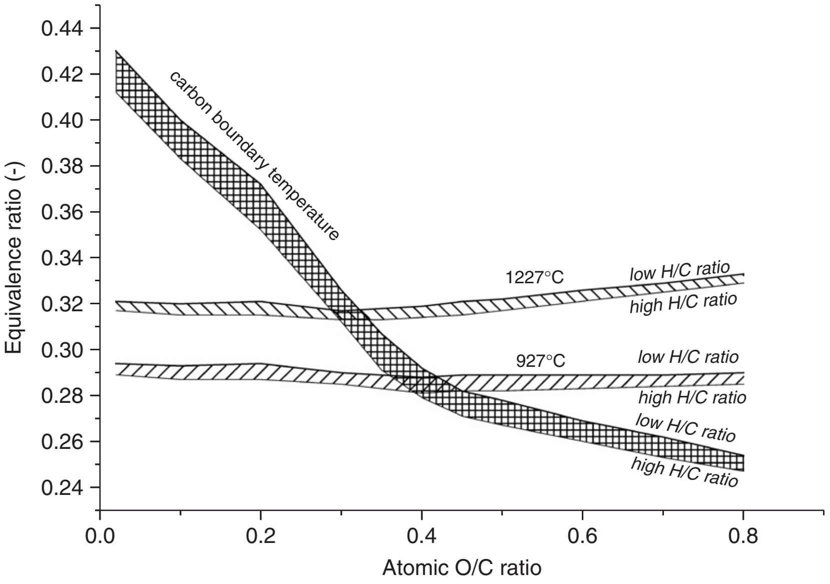

Fig. 5. Minimum equivalence ratios for gasification of fuels of varying O/C and H/C ratios at different temperatures.

Carbon gasification:

$$C + 1/2O_2 = CO. \tag{13}$$

Carbon combustion:

$$C + O_2 = CO_2. \tag{14}$$

As expected, it becomes clear from Fig. 5 that coal gasifiers operated at the carbon boundary temperature require much higher equivalence ratios than biomass gasifiers. For fuels with O/C ratios above 0.4 (corresponding to carbon boundary temperatures below 927 °C), the required equivalence ratio increases only moderately with decreasing O/C ratios. This happens because the increased extent of oxidation is accompanied by an increased extent of reforming, as the reaction equilibria of Eqs. (9) and (10) become more favorable at higher temperature. If gasification is carried out at a fixed reference temperature, the difference in equivalence ratios levels out. The equivalence ratios become fairly constant for all fuels, around 0.29 for a gasification temperature of 927 °C and 0.32–0.33 for a gasification temperature of 1227 °C. At low O/C ratios, steam partly replaces oxygen, so that lower equivalence ratios are sufficient, whereas at high O/C ratios, more oxygen is required to reach the desired temperatures. In other words, biomass is gasified above its carbon boundary temperature by over-oxidizing the fuel, where coal may be gasified below its carbon boundary temperature by moderation with steam.

4.2. Gasification efficiencies

Fig. 6a shows the thermodynamic efficiencies corresponding to oxygen-blown gasification of fuels with different O/C and H/C ratios. For gasification at the carbon boundary

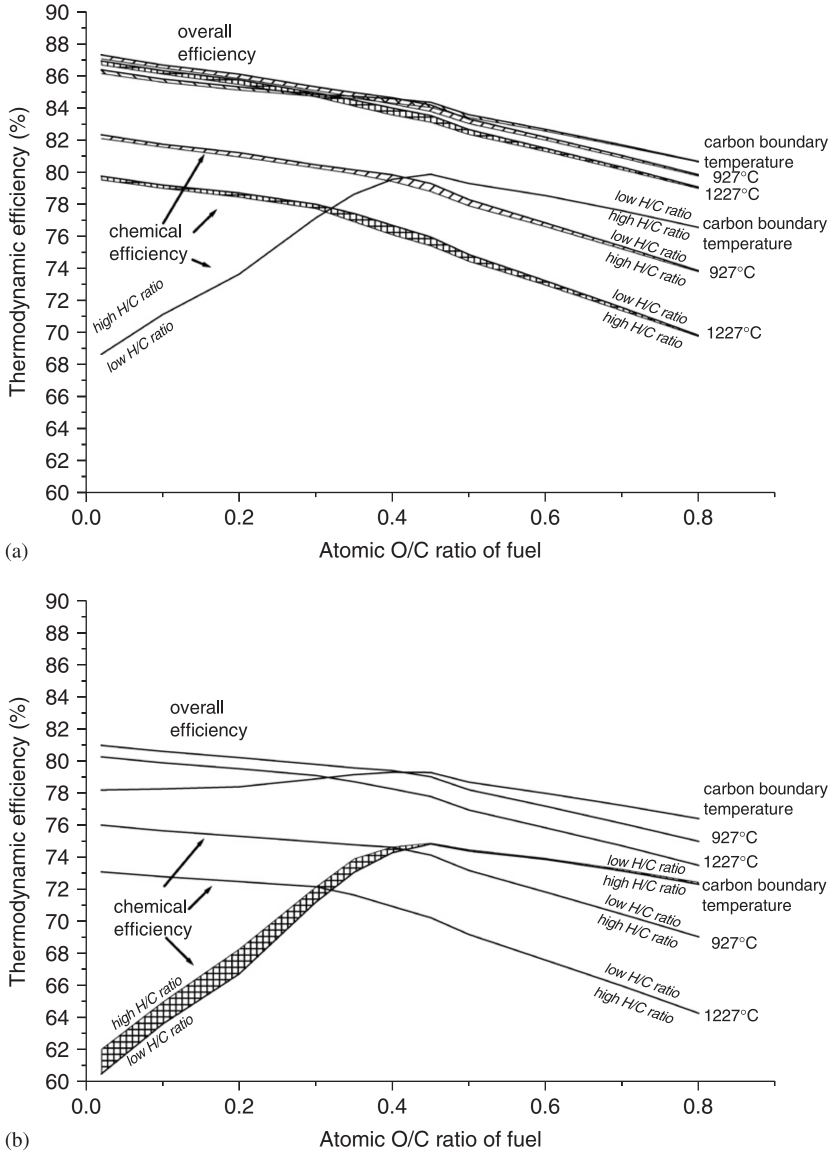

Fig. 6. (a) Thermodynamic efficiency of gasification of fuels of varying O/C and H/C ratios at different temperatures. (b) Thermodynamic efficiency of gasification, including steam and oxygen production, of fuels of varying O/C and H/C ratios at different temperatures.

temperature, the overall efficiency as well as chemical efficiency rises when decreasing the *O*/*C* ratio from 0.8 to 0.4. Beyond this point, the overall efficiency increases only marginally, whereas the chemical efficiency decreases. This is caused by the sharp temperature increase at *O*/*C* ratios below 0.4 (see Fig. 4), which results in a high physical exergy of the product gas, but low chemical exergy. For gasification at 927 °C, respectively, 1227 °C, the chemical efficiency in the *O*/*C* region below 0.4 is improved substantially due to moderation of the temperature with steam, with the chemical efficiency at 927 °C approximately 2% points higher than at 1227 °C. Moderation of temperature hardly changes the overall efficiency. For fuels with high *O*/*C* ratios, such as biomass, the efficiencies at a gasification temperature of 927 or 1227 °C are considerably lower than at the carbon boundary temperature. These fuels need to be over-oxidized in order to reach the desired gasification temperature. Therefore, more oxygen is used than necessary for complete gasification, which causes thermodynamic losses.

Fig. 6b shows thermodynamic efficiencies for gasifying fuels of varying composition, when exergetic losses for production of oxygen, electricity and steam are taken into account. The effect of these additional exergetic losses is substantial. The losses incurred for producing oxygen are most obvious for gasification of fuels with low *O*/*C* ratios at the carbon boundary temperature, which need high equivalence ratios to be gasified. The curves for overall and chemical efficiency flatten somewhat; this happens below an *O*/*C* ratio of 0.4 for gasification at 927 °C and an *O*/*C* ratio of 0.3 for gasification at 1227 °C.

4.3. Process losses

Fig. 7 shows, as an illustration, the relative exergy losses for gasification at 927 °C. Apart from exergy losses occurring in sub-processes in the gasifier, also exergy losses for production of oxygen, electricity and steam are shown. The exergy losses due to heating of fuel and chemical reaction are by far the largest contribution to the overall exergy losses. These losses correlate very well with β, the ratio of chemical exergy to lower heating value. Therefore, it can be concluded that fuels with a low β are preferred in order to achieve high exergetic efficiency.

Exergy losses due to oxygen and electricity production consume 5–6% of the fuel's exergy. These losses increase only slightly with decreasing *O*/*C* ratio because the required equivalence ratio is nearly constant. Fig. 7 explains the slight flattening of efficiency curves below an O/C ratio of 0.4, observed in Fig. 6b. Below this ratio, steam is introduced to moderate the gasification temperature. Although the exergetic losses due to heating of fuel and chemical reaction continue to decrease below 0.4, these are partially compensated by the losses incurred for steam production, and to a smaller extent for heating of steam and mixing of reactant gases.

5. Conclusion and discussion

It was shown that the presence of kinetically limited char gasification reactions in gasifiers negatively influences the efficiency of a gasifier. Therefore, a relatively simple equilibrium model predicts the maximum efficiency that could be attained.

In order to gasify fuels with high thermodynamic efficiency at atmospheric pressure, it is recommended to use a gasification temperature around 927 °C, and fuels with *O*/*C* ratio smaller than 0.4 (corresponding to a preferred lower heating value above 23 MJ/kg). To minimize kinetic restrictions, higher temperatures may be preferred. At a gasification temperature of 1227 °C, the

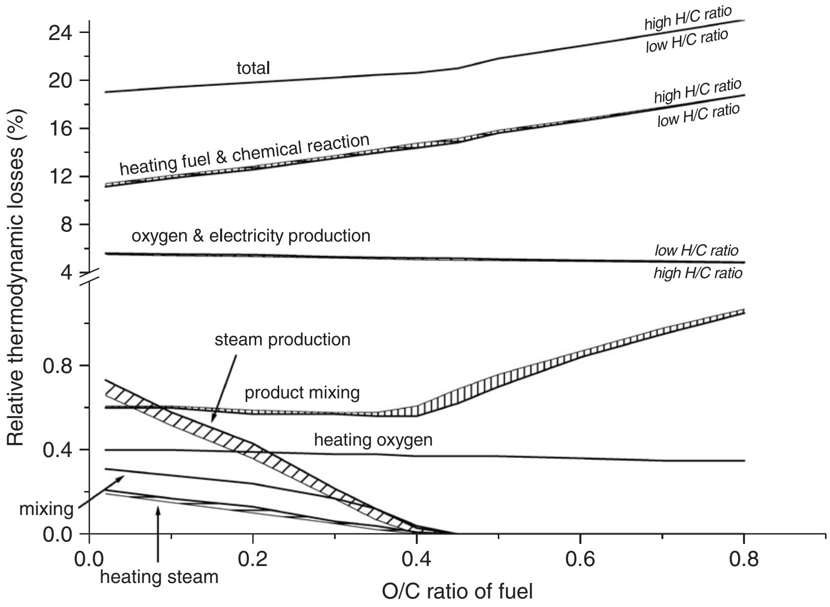

Fig. 7. Relative exergy losses for sub-processes in gasification of fuels (including steam and oxygen production) of varying *O*/*C* and *H*/*C* ratios at 927 °C.

recommended O/C ratio of the fuel is 0.3 or less (corresponding to a preferred lower heating value above 26 MJ/kg). Fuels with higher O/C ratios, such as wood, have larger exergy losses because of their high ratio of chemical exergy to lower heating value. Furthermore, such fuels are over-oxidized in the gasifier in order to reach the required gasification temperature. In practice, due to heat losses, the presence of ash in the fuel, and of nitrogen in the gasifying agent if air or enriched air is used, the extent of over-oxidation will be more severe. However, for gasification at elevated pressures, the minimum temperature required for gasification increases, and the gap with kinetically preferred temperatures (i.e. the extent of over-oxidation) can be reduced.

Based on the above, it becomes clear that highly oxygenated biofuels are not ideal fuels for gasifiers from an exergetic point of view. However, this is a purely theoretical conclusion, based on thermodynamic equilibrium and 100% carbon conversion, which does not imply that woody biomass is less attractive than coal as a gasification fuel. Apart from the composition of the organic matter in a fuel, there are many other factors that need to be taken into consideration, such as the lower ash, sulfur and nitrogen content of biomass and the high reactivity of biomass char compared to coal char. In practice, at the same temperature, biomass gasification may have a higher carbon conversion than coal gasification, which means that kinetic restrictions may outweigh the potential thermodynamic advantage of coal over biomass.

What this study does teach us is that methods to modify the properties of solid biofuels prior to gasification could be considered. An effective way to do so, is mixing of biomass with coal (co-gasification, see e.g. [30]), a process with negligible additional irreversibilities. Alternatively, wood could be separated into its components, e.g. by extraction of lignin with phenol, and only the lignin component could be gasified. However, this greatly reduces the amount of fuel available for gasification, and would be attractive only if the C5 and C6 polysugars present in the cellulose and hemi-cellulose fractions are desired products. Another approach uses thermal pretreatment of wood at temperatures around 250 °C (a process known as biomass torrefaction [31]), which lowers the O/C ratio prior to gasification. Additional irreversibilities in the extra process step must be carefully taken into account [32]. Lignin or torrefied wood could also be mixed with coal to enhance the gasification fuel properties further.

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Appendix A. Gasification efficiency at equilibrium and nonequilibrium conditions

Fig. 8a illustrates gasification of biomass at equilibrium conditions at typical gasification temperature of 877 °C. Preheating of fuel or gasifying medium is not considered, which means that the fuel and oxygen enter the gasifier at a temperature $T_0 = 25\,^{\circ}\mathrm{C}$. The biomass fuel is represented by a general formula of $CH_{1.4}O_{0.6}$ (with net heat of combustion of 19.6 MJ/kg) and indicated by point A in the triangular diagram. Assuming that 10% moisture is present in the fuel, the composition of the wet biomass is given by point B. When oxygen is added, the composition moves into the direction of point C; at this point, all carbon is present in the gaseous phase as carbon monoxide, carbon dioxide or methane. The required equivalence ratio, defined as the amount of oxygen added for gasification relative to the amount of oxygen required for complete combustion, is 0.295. Notice that point C does not lie on the carbon boundary line (line I), because this line has to be crossed over in order to reach the desired temperature. The thermodynamic efficiency of air or oxygen-blown gasification, based on the first and second law of thermodynamics, reaches a maximum at the carbon boundary temperature

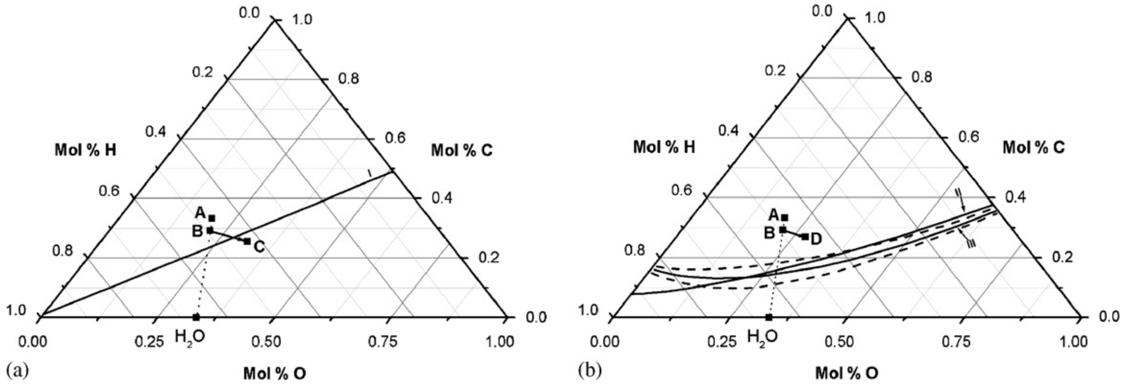

Fig. 8. Biomass ($CH_{1.4}O_{0.6}$, point A), wet biomass (containing 10 wt% moisture, point B) and gasification of wet biomass, (a) at equilibrium conditions (to point C) and (b) at nonequilibrium conditions (to point D).

[8]. Theoretically, the biomass could be gasified more efficiently at a slightly lower equivalence ratio.

The triangular diagram in Fig. 8b shows the carbon boundary lines that we have determined, based on the research of Li et al. (line II; this is the carbon boundary line at 627 °C) and the research of Kersten (line III; including lines to indicate uncertainty). These lines have shifted downwards compared to line I in Fig. 8a, which indicates that as a result of kinetic limitations, more oxygen is required for complete gasification. This is the combined net result of two effects. If the exothermic reaction of Eq. (8) is kinetically limited and more methane (and higher hydrocarbons) is formed than predicted, it is favorable because hydrocarbon formation contributes to the carbon conversion. However, if the endothermic reactions of Eqs. (9) and (10) are also kinetically limited, it is not favorable because this means that these reactions are effectively 'frozen in', and more oxygen must be added to obtain complete carbon conversion.

Fig. 8b illustrates gasification of biomass at a gasification temperature of 877 °C at quasi-equilibrium conditions, with the reaction equilibria evaluated at 627 °C. Again, the biomass fuel considered in this work is represented by a general formula of $CH_{1.4}O_{0.6}$, indicated by point A in the triangular diagram, and the composition of the wet biomass including 10% moisture is given by point B. When oxygen is added, the composition moves into the direction of point D. At this point, 60% of the carbon is present in the gaseous phase and 40% remains unconverted. Due to the low carbon conversion, the required equivalence ratio to reach the desired process temperature is only 0.151, which is lower than for the unmodified equilibrium model. This is because the endothermic char reforming reactions, which normally act as a temperature ceiling in a gasifier, hardly occur. In practice, higher equivalence ratios need to be used to compensate for heat losses from the gasifier and warm up inert components (such as ash in fuel, and nitrogen if air is used as gasifying medium). More carbon is thus converted, but the total carbon conversion in fluidized bed gasifiers operating at atmospheric pressure and bed temperatures below 910 °C remains rather low, in the range of 70–85% at equivalence ratios of 0.2–0.3 and complete carbon conversion only above 0.4 [23].

The process parameters for atmospheric gasification at a temperature of 877 °C at equilibrium and quasi-equilibrium conditions are compared in Table 2. The gas composition is very different for these scenarios. At quasi-equilibrium conditions, much less carbon monoxide is present in the gas, and more methane, steam and carbon dioxide. Methane formed in gasifiers, probably by thermal cracking of tar, reforms too slowly and hence its concentration is higher than at equilibrium conditions. The concentrations of steam and carbon dioxide are higher due to kinetic limitations of the char reforming reactions.

Table 2
Gasification at 877 °C, equilibrium and quasi-equilibrium conditions

	Equilibrium conditions	Quasi-equilibrium conditions
Equivalence ratio	0.295	0.151
Carbon conversion (%)	100	60
Gas composition (mol%)		
H_2O	9.6	17.9
H_2	36.0	37.0
CO	44.3	19.5
CO_2	10.0	21.3
CH_4	< 0.1	4.3
Gasifier efficiency (%)		
Chemical	75.2	70.3
Physical	5.5	6.7
Total	80.7	77.0
Process losses (%)		
Heating oxygen	0.4	0.3
Heating fuel and chemical reaction	17.9	21.4
Product mixing	1.0	1.3
Gasification system efficiency (%)		
Total	75.6	73.0
Total if unconverted carbon is lost		48.7

Table 2 compares the thermodynamic efficiency of the gasification processes. It shows that the thermodynamic efficiency is highest at equilibrium conditions. For the gasifier, the process losses amount to 19.3% for the equilibrium case and 23.0% for the quasi-equilibrium case. Due to losses incurred for oxygen production, these numbers are higher for the total gasification systems, but the conclusion that the equilibrium case is more efficient still holds. Analysis of the process losses, also shown in Table 2, indicates that the losses for heating the fuel and chemical reaction have the largest contribution. These losses are higher for the quasi-equilibrium case. The reason that gasification at equilibrium conditions is more efficient is that the exothermic oxidation reactions are effectively coupled with endothermic reforming reactions, so that the driving force for the overall chemical reaction (difference in chemical potential) is lower.

In the definitions of Eqs. (5) and (6), unconverted carbon is not regarded as a loss because, in principle, it can be recycled into the gasifier. However, this is problematic in practice as unconverted carbon is contained in the ashes. If unconverted carbon is regarded as a loss, the thermodynamic efficiency for gasification at quasi-equilibrium conditions drops below 50%. This number may be somewhat improved by processing the unconverted carbon rather than to dispose of it, e.g. it can be burned out in a separate reactor.

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